

AD-A104 748

YORK UNIV DOWNSVIEW (ONTARIO) DEPT OF CHEMISTRY
ELECTROCHEMISTRY OF MAIN-GROUP PHTHALOCYANINES. (U)
JUL 81 A B LEVER, P C MINOR

F/6 7/4

N00014-78-C-0592

UNCLASSIFIED

TR-17

NL

1 x 1
100 x 100



END
DATE
FILMED
10-81
DTIC

AD A104748

OFFICE OF NAVAL RESEARCH

Contract ⁽¹⁵⁾ N00014-78-C-0592

Task No. NR 051-693

TECHNICAL REPORT NO. 17

⁽⁶⁾ ELECTROCHEMISTRY OF MAIN-GROUP PHTHALOCYANINES.

BY

⁽¹⁰⁾ A.B.P./Lever ~~and~~ P.C./Minor

Prepared for Publication

in

Inorganic Chemistry

York University

Department of Chemistry

Downsview (Toronto)

Ontario M3J-1P3

July 30, 1981

DTIC
ELECTE
SEP 29 1981
H

⁽¹²⁾ 9/

⁽¹¹⁾ 30 JUL 81

Reproduction in whole or in part is permitted for
any purpose of the United States Government.

This document has been approved for public release
and sale; its distribution is unlimited.

DTIC FILE COPY

87 9 28 162

422042

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 17	2. GOVT ACCESSION NO. AD-A104 748	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ELECTROCHEMISTRY OF MAIN-GROUP PHTHALOCYANINES		5. TYPE OF REPORT & PERIOD COVERED Interim Report-- Sept. 80 - July 81
7. AUTHOR(s) A.B.P. Lever* and P.C. Minor		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry York University, 4700 Keele Street, Downsview, (Toronto), Ontario, M3J 1P3. Canada		8. CONTRACT OR GRANT NUMBER(s) N00014-78-C-0592
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N. Quincy Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE July 30, 1981
		13. NUMBER OF PAGES 2
		15. SECURITY CLASS. (of this report) Unclassified
		16a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Prepared for publication in: INORGANIC CHEMISTRY		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Electrochemistry, Phthalocyanines		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The oxidation and reduction potentials of main group metallophthalocyanines are shown to follow a linear relationship with the function $r/(ze)$ (radius/charge). This relationship may be used to facilitate the design of photocatalysts with specific redox potentials.		

DD FORM 1473
1 JAN 73

EDITION OF 1 NOV 68 IS OBSOLETE
S/N 0102-014-6601

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Electrochemistry of Main-Group Phthalocyanines

A. B. P. Lever* and P. C. Minor

Received February 5, 1981

Metallophthalocyanines have been the subject of several electrochemical investigations,¹⁻⁹ but no systematic study as a function of central metal ion has been published. We have recently completed a study of the electrochemistry of main-group phthalocyanines with a view of providing a basis for the design of photoredox catalysts. Differential-pulse polarography and cyclic voltammetry were employed to identify the energies of the various redox couples. We are concerned here with the first ring reduction and first ring oxidation. For most couples, these processes were reversible or quasi-reversible in the medium (DMF/TEAP) employed.

A well-defined relationship was observed between the first ring reduction, or oxidation, and the size and charge of the central metal ion. This information is of special value of those interested in the potential use of phthalocyanines as photocatalysts.

Experimental Section

The main-group metallophthalocyanines were prepared and purified by well-established literature methods.¹⁰ Electrochemical data were recorded with Princeton Applied Research Models 173, 174A, 175, a Houston Model 9002A XY recorder, and Tektronix 5103N storage oscilloscope. A standard calomel electrode was used as a reference (with Luggin capillary) and platinum wire used as working and counterelectrodes. Dimethylformamide (Fisher, "Spectranalysed"), and tetraethylammonium perchlorate (Eastman, recrystallized several times) were used as solvent and supporting electrolyte, respectively. Details of our electrochemical procedures have been previously published.³

Discussion

Redox couples for a range of main-group metallophthalocyanines are shown in Table I. A well-defined pattern is readily apparent. (i) The metal phthalocyanines with the more positive central metal ions are more difficult to oxidize. (ii) The phthalocyanine anions with the more positive central metal ions are more difficult to oxidize, i.e., their neutral species are easier to reduce. (iii) From comparison of the dispositive or tripositive ions, the smaller the ion, the easier is the species to reduce, and the more difficult to oxidize. (iv) Elements with especially large radii, specifically lead and mercury, have anomalous redox energies; these ions presumably sit outside the phthalocyanine ring and do not then fit into the well-behaved series of complexes.

Observations i-iii lead to the supposition that these redox energies are functions of the polarizing power of the central metal ion, expressible as charge/radius (ze/r). Increasing polarizing power of the central metal ion causes an increase in the potential at which the phthalocyanine or phthalocyanine anion is oxidized.

There are a variety of metal ion radii available in the literature. We have chosen to use the effective ionic radii of Shannon and Prewitt¹¹ because their list contains a fairly complete set of radii shown as a function both of valency and coordination number.

The coordination numbers of these species are not unambiguously known, but it is likely that most of the complexes will be solvated to form six-coordinate derivatives in solution in DMF.

Since these main-group species are all closed-shell ions, we have used the formal charge ($2+$ or $3+$) to generate (ze/r) values shown in Table I.

A plot of these quantities, E° vs. ze/r , is curved. A linear plot is conveniently obtained by plotting E° against (r/ze) and

is shown in Figure 1 for both phthalocyanine reduction and oxidation. The linearity of both plots is striking. The equations of the lines are as follows: oxidation, $(ze/r)(E^\circ - 1170) = -11.7$; reduction, $(ze/r)(E^\circ + 385) = -12.0$. E° is relative to the standard calomel electrode.

Table I. Main-Group Phthalocyanine Reduction and Oxidation Couples (mV vs. SCE)

metal	radius, pm	ze/r	$E^\circ_{\text{Ox}}{}^a$, mV	$E^\circ_{\text{Red}}{}^a$, mV	$E^\circ_{\text{Ox}} - E^\circ_{\text{Red}}$, mV
(O ³⁺ Am) ₂ Si ^{IV}	54	0.074		-540	
ClAl ^{III}	67.5	0.044	915	-655	1570
ClGa ^{III}	76	0.040	865	-735	1600
ClIn ^{III}	94	0.032	830	-715	1545
Mg ^{II}	86	0.023	650	-930	1580
Zn ^{II}	88	0.023	685	-900	1585
Cd ^{II}	109	0.018	540	-1170 ^b	1710
Hg ^{II} ^b	110	0.018	250	-1305	1555
Pb ^{II} ^b	133	0.015	670	-720	1390

^a Potentials quoted to nearest 5 mV. ^b These data were not included in the derivation of the equation of the line. Where previous data exist, agreement is satisfactory.^{1,9}

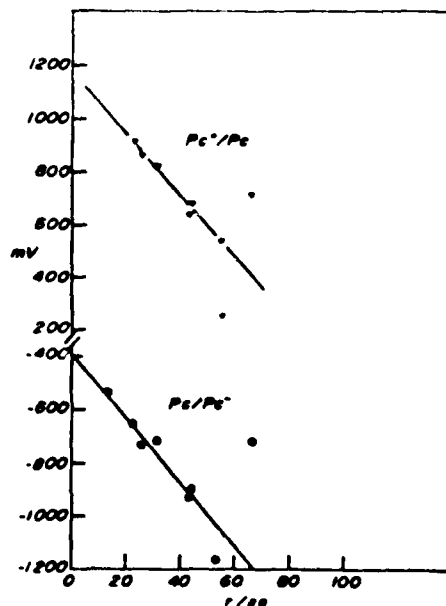



Figure 1. Main-group phthalocyanine oxidation and reduction potentials plotted as a function of r/ze . Points lying off the lines are for the large ions Pb(II), Hg(II), and Cd(II) (reduction only) which do not lie within the phthalocyanine ring.

Although the least-squares plots do not show that the lines are strictly parallel, the deviation therefrom is small. For most species the difference in potential between ring reduction and oxidation is close to 1570 mV.

Provided that the metal ion sits inside the phthalocyanine ring, these correlations provide a method of estimating main-group phthalocyanine redox potentials. Interestingly, the limit of phthalocyanine oxidation and reduction appears to be +1170 and -385 mV (vs. SCE), respectively, as (r/ze) approaches 0. All main-group phthalocyanines should fall within these confines, provided  inside the phthalocyanine ring.


Successive oxidation and reduction potentials (e.g., second and third reductions) can be estimated from the established intervals between these various processes.⁴

Transition-metal phthalocyanines follow a similar trend.^{5,12} For a given valency where, within the first-row transition series the size of the metal ion does not change greatly, the reduction potential depends upon the valency. Thus Cr(II), Mn(II), Ni(II), and Cu(II) phthalocyanines all reduce at essentially the same potential (ca. -0.84 vs. SCE) anodic of M(I) species such as Fe(I) and Co(I) and cathodic of M(IV) species such as TiO and VO.¹²

The use of these data in the design of photoredox catalysts will be the subject of a future communication.¹³

Acknowledgment. This research is part of a joint project with Professor A. J. Bard (University of Texas at Austin) funded by the Office of Naval Research, to whom we are indebted. We also thank Professor I. M. Walker for useful discussion.

- (1) Wolberg, A.; Manassen, J. *J. Am. Chem. Soc.* 1970, 92, 2982.
- (2) Rollman, L. D.; Iwamoto, R. T. *J. Am. Chem. Soc.* 1968, 90, 1455.
- (3) Lever, A. B. P.; Wilshire, J. P. *Can. J. Chem.* 1976, 54, 2514.
- (4) Clack, D. W.; Hush, N. S.; Woolsey, I. S. *Inorg. Chim. Acta* 1976, 19, 129.
- (5) Lever, A. B. P.; Wilshire, J. P. *Inorg. Chem.* 1978, 17, 1145.
- (6) Kadish, K. M.; Bottomley, L. A.; Cheng, J. S. *J. Am. Chem. Soc.* 1978, 100, 2731.
- (7) Fanning, J. C.; Park, G. B.; Jones, C. G.; Heatley, W. R., Jr. *J. Inorg. Nucl. Chem.* 1980, 42, 343.
- (8) Lever, A. B. P.; Minor, P. C. *Adv. Relax. Inter. Processes*, 1980, 18, 115.
- (9) Leza, D.; Reix, M. *J. Him. Phys.* 1974, 71, 511.
- (10) Lever, A. B. P. *Adv. Inorg. Chem. Radiochem.* 1965, 7, 27.
- (11) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B* 1969, B25, 925.
- (12) Lever, A. B. P.; Licoccia, S.; Magnell, K.; Minor, P. C.; Ramaswamy, B. C. *ACS Symp. Ser.*, in press.
- (13) Lever, A. B. P.; Licoccia, S.; Ramaswamy, B. S.; Kandil, A.; Styron, D. V., accepted for publication in *Inorg. Chim. Acta*.

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Special
A	

TECHNICAL REPORT DISTRIBUTION LIST, CEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Area Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
ONR Western Regional Office 1030 East Green Street Pasadena, California 91106	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
ONR Eastern/Central Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, 350

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. A. B. Ellis Chemistry Department University of Wisconsin Madison, Wisconsin 53706	1	Dr. R. P. Van Duyne Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. M. Wrighton Chemistry Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. B. Stanley Pons Department of Chemistry University of Alberta Edmonton, Alberta CANADA T6C 2G2	1
Larry F. Plew Naval Weapons Support Center Code 30735, Building 2906 Crane, Indiana 47522	1	Dr. Michael J. Weaver Department of Chemistry Michigan State University East Lansing, Michigan 48824	1
S. Ruby DOE (STOR) 600 E Street Washington, D.C. 20545	1	Dr. R. David Rauh EIG Corporation 55 Chapel Street Newton, Massachusetts 02158	1
Dr. Aaron Wold Brown University Department of Chemistry Providence, Rhode Island 02192	1	Dr. J. David Margerum Research Laboratories Division Hughes Aircraft Company 3011 Malibu Canyon Road Malibu, California 90265	1
Dr. R. C. Chudacek McGraw-Edison Company Edison Battery Division Post Office Box 28 Bloomfield, New Jersey 07003	1	Dr. Martin Fleischmann Department of Chemistry University of Southampton Southampton SO9 5NH England	1
Dr. A. J. Bard University of Texas Department of Chemistry Austin, Texas 78712	1	Dr. Janet Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. M. M. Nicholson Electronics Research Center Rockwell International 3370 Miraloma Avenue Anaheim, California	1	Dr. R. A. Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. Donald W. Ernst Naval Surface Weapons Center Code R-33 White Oak Laboratory Silver Spring, Maryland 20910	1	Mr. James R. Moden Naval Underwater Systems Center Code 3632 Newport, Rhode Island 02840	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. Paul Delahay Department of Chemistry New York University New York, New York 10003	1	Dr. P. J. Hendra Department of Chemistry University of Southampton Southampton SO9 5NH United Kingdom	1
Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 44106	1	Dr. Sam Perone Department of Chemistry Purdue University West Lafayette, Indiana 47907	1
Dr. D. N. Bennion Department of Chemical Engineering Brigham Young University Provo, Utah 84602	1	Dr. Royce W. Murray Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514	1
Dr. R. A. Marcus Department of Chemistry California Institute of Technology Pasadena, California 91125	1	Naval Ocean Systems Center Attn: Technical Library San Diego, California 92152	1
Dr. J. J. Auborn Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. C. F. Mueller The Electrochemistry Branch Materials Division, Research & Technology Department Naval Surface Weapons Center White Oak Laboratory Silver Spring, Maryland 20910	1
Dr. Adam Heller Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. G. Goodman Globe-Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. T. Katan Lockheed Missiles & Space Co, Inc. P.O. Box 504 Sunnyvale, California 94088	1	Dr. J. Boechler Electrochimica Corporation Attention: Technical Library 2485 Charleston Road Mountain View, California 94040	1
Dr. Joseph Singer, Code 302-1 NASA-Lewis 21000 Brookpark Road Cleveland, Ohio 44135	1	Dr. P. P. Schmidt Department of Chemistry Oakland University Rochester, Michigan 48063	1
Dr. B. Brummer EIC Incorporated 55 Chapel Street Newton, Massachusetts 02158	1	Dr. H. Richtol Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181	1
Library P. R. Mallory and Company, Inc. Northwest Industrial Park Burlington, Massachusetts 01803	1		

SP472-3/A3

472:GAN:716:ddc
78u472-608

TECHNICAL REPORT DISTRIBUTION LIST, GEN

No.
Copies

Dr. Rudolph J. Marcus
Office of Naval Research
Scientific Liaison Group
American Embassy
APO San Francisco 96503

1

Mr. James Kelley
DTNSRDC Code 2803
Annapolis, Maryland 21402

1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. R. Nowak Naval Research Laboratory Code 6130 Washington, D.C. 20375	1	Dr. John Kincaid Department of the Navy Strategic Systems Project Office Room 901 Washington, DC 20376	1
Dr. John F. Houlihan Shenango Valley Campus Pennsylvania State University Sharon, Pennsylvania 16146	1	M. L. Robertson Manager, Electrochemical Power Sonices Division Naval Weapons Support Center Crane, Indiana 47522	1
Dr. M. G. Sceats Department of Chemistry University of Rochester Rochester, New York 14627	1	Dr. Elton Cairns Energy & Environment Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	1
Dr. D. F. Shriver Department of Chemistry Northwestern University Evanston, Illinois 60201	1	Dr. Bernard Spielvogel U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709	1
Dr. D. H. Whitmore Department of Materials Science Northwestern University Evanston, Illinois 60201	1	Dr. Denton Elliott Air Force Office of Scientific Research Bldg. 104 Bolling AFB Washington, DC 20332	1
Dr. Alan Bewick Department of Chemistry The University Southampton, SO9 5NH England	1		
Dr. A. Himy NAVSEA-5433 NC #4 2541 Jefferson Davis Highway Arlington, Virginia 20362	1		

**DAT
FILM**